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A STUDY OF THERMODYNAMIC PHASE STABILITY OF INTERMETALLIC THIN FILMS OF Pt_2Ga, PtGa AND $PtGa_2$ ON GALLIUM ARSENIDE

by

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Epitaxial thin films of three different ~~Pt-Ga~~ intermetallic compounds have been grown on ~~GaAs~~ by molecular beam epitaxy (MBE). The resultant films have been annealed at various temperatures and then examined using x-ray two-theta diffraction. Both $PtGa_2$ and PtGa thin films are chemically stable on GaAs under 1 atmosphere of N_2 up to 450°C and 600°, respectively. Thin films of Pt_2GA react with GaAs at temperatures as low as 200°C to form phases with higher Ga concentration.

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ABSTRACT

Epitaxial thin films of three different Pt-Ga intermetallic compounds have been grown on GaAs by molecular beam epitaxy (MBE). The resultant films have been annealed at various temperatures and then examined using X-ray two-theta diffraction. Both $PtGa_2$ and PtGa thin films are chemically stable on GaAs under 1 atmosphere of N_2 up to 450°C and 600°C, respectively. Thin films of Pt_2Ga react with GaAs at temperatures as low as 200°C to form phases with higher Ga concentration.

Introduction

The interface chemistry of metal-semiconductor contacts plays an important role in controlling the electrical properties of Schottky barriers and Ohmic contacts [1]. Chemically stable contacts must be formed at the metal-semiconductor interface in order for electronic devices to survive processing procedures and operate reliably in harsh environment applications for long periods of time [2,3]. A possible solution for this interface problem would be to use a contact metal that can coexist with GaAs in bulk thermodynamic equlibrium. Such stable metals can be found by examining ternary phase diagrams, such as the Pt-Ga-As system, which was experimentally elucidated by Tsai et. al. [4] and is illustrated in Fig. 1. The existence of a pseudobinary tie-line between two compounds in the ternary phase diagram implies that the compounds will not react with each other in a closed system, i.e. the bulk compounds are in thermodynamic equilibrium with respect to each other. Therefore, from Fig. 1 it can be expected that PtGa and $PtGa_2$ will form stable contacts with GaAs but that Pt_2Ga will not. In the present study, these expectations are tested by investigating the phase composition of thin films of Pt_2Ga, PtGa and $PtGa_2$ on GaAs after annealing to various temperatures.

Film Growth

The Pt-Ga intermetallic films were grown in a MBE chamber with a base pressure of 2×10^{-10} torr and a deposition pressure of approximately 4×10^{-9} torr. The two inch GaAs substrates were introduced via a cryopumped load lock system and mounted on a modified manipulator equipped with radiative heating elements. The samples were cleaned in-situ by heating to a temperature of approximately 525°C. The platinum was evaporated using a Varian 3 KW electron beam evaporator and the gallium was obtained from a Knudsen cell constructed of a pyrolytic boron nitride (PBN) crucible with a tantalium heating element. The fluxes of platinum and gallium were initially tuned to the proper stoichiometry based on empirical knowledge. $PtGa_2$ can be visually identified by its characteristic golden color, since $PtGa_2$ is the only Pt-Ga phase that has a band structure similar to that of elemental gold [5]. Neither PtGa nor Pt_2Ga can be easily identified by color. The flux rate from the gallium source was stabilized by temperature control circuits that ensured a constant flux rate for each source power setting. Subsequent depositions have been controlled with a Leybold-Inficon IC-6000 crystal monitor system. To obtain single phase Pt-Ga intermetallic films, the flux ratio of gallium to platinium was adjusted to be slightly Ga rich. Co-evaporation of each Pt-Ga intermetallic proceeded with the substrate held at temperatures ranging from near room temperature to over 500°C at epilayer growth rates ranging from approximately 0.5 to 5 microns/hour.

Composition Analysis

XRD patterns of the films were taken on a Phillips X-ray powder diffractometer, which was interfaced to a microcomputer that controlled the scan rate and collected data at 0.1° intervals with a counting time of 10 seconds at each angle. The total time required for a complete scan (2θ from 10° to 100°) was about 3 hours and the typical signal-to-noise ratio for a strong diffraction peak was 30 to 1. The d spacings of the $PtGa_2$ and Pt_2Ga thin films were checked against a reference tabulation [6] to ensure that they were identified correctly. As

no known PtGa JCPDS data exists, the known d-spacings of PtGa [7] were compared with values calculated from the diffraction pattern of the thin film and were found to agree closely. The thin films were annealed for twenty minutes in a quartz tube furnace under a nitrogen atmosphere for temperatures ranging from 100°C to 800° C. In this paper, we present XRD results of annealing studies of the Pt-Ga intermetallic single phase thin films. A complete characterization of these films, including Auger electron spectroscopy (AES) and X-ray photoemission spectroscopy (XPS), will be presented elsewhere [8].

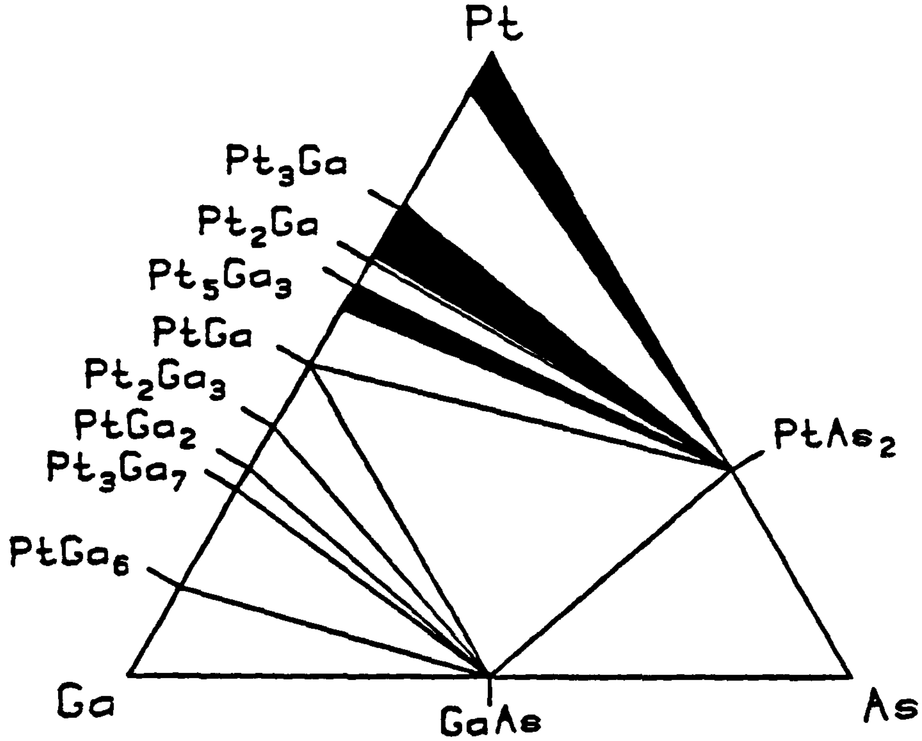

Fig. 1. Solidus portion of the Pt-Ga-As ternary phase diagram at 25°C.

Results and discussion

The grown films were specular, both to the eye and by optical microscopy. Fig. 2 shows typical powder XRD patterns of the three types of intermetallic single phase Pt-Ga thin films grown on GaAs (001) in the as-deposited state. The PtGa and Pt_2Ga thin films have a dominant (210) and (112) reflection, respectively. The $PtGa_2$ thin films displayed roughly equal intensity (111), (220) and (311) reflections. This would seem to imply that the crystal quality of PtGa and Pt_2Ga thin films is better than that of $PtGa_2$ films in spite of larger lattice mismatches. XRD patterns of a sample of Pt_2Ga on GaAs annealed to 500°C are shown in Fig. 3. Even at 200°C, a new peak corresponding to the PtGa (210) reflection begins to appear at $2\theta = 41.4°$. In the diffraction patterns of the film heated to high temperatures, new phases, such as $PtGa_2$ and $PtAs_2$, begin to form at 300°C and all peaks corresponding to the Pt_2Ga phase eventually disappeared at 500°C. According to the Pt-Ga-As ternary phase diagram, Pt_2Ga is expected to react with GaAs to produce $PtAs_2$ and PtGa, because there is no tie-line between Pt_2Ga and GaAs. However, annealing in an open system may cause As evaporation resulting from thermal decomposition of $PtAs_2$ and GaAs. With further loss of As, other Pt-Ga intermetallic compounds, such as $PtGa_2$ and Pt_3Ga_7, may be produced. This prediction agrees very well with the experimental results; all the peaks correspond to PtGa, $PtGa_2$, Pt_3Ga_7 and $PtAs_2$ in the diffraction pattern of the Pt_2Ga thin films on GaAs annealed to 500°C.

Fig. 4 shows XRD patterns of PtGa on a GaAs sample in the as-deposited state and after annealing at various temperatures for 20 minutes each. The diffraction pattern of the PtGa film annealed to 200°C shows that a small peak corresponding to Pt_2Ga (112) beside the PtGa (210) disappeared and the other PtGa peaks became sharper and more intense. This implies that a small amount of unstable Pt_2Ga phase in the PtGa thin film reacted with extra Ga in the film or with the substrate. Annealing improves the crystallinity of the PtGa

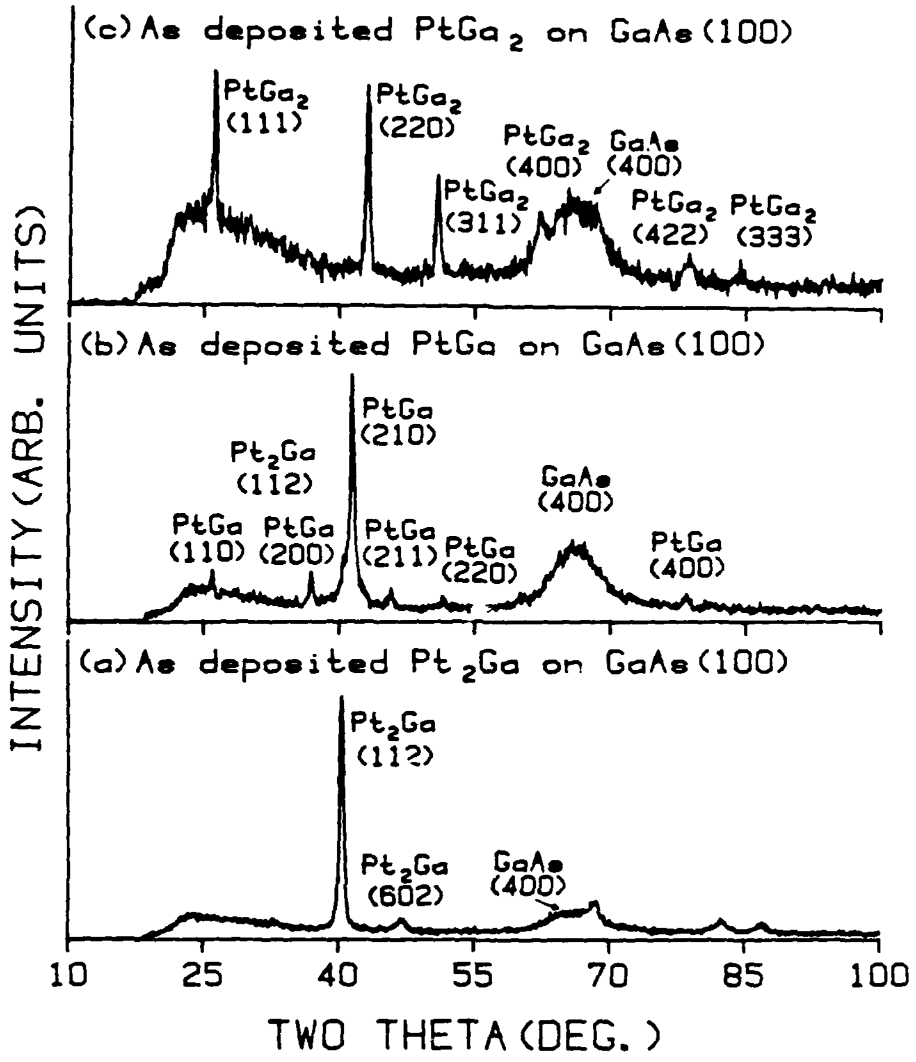

Fig. 2. XRD patterns of the three types of intermetallic single phase Pt-Ga thin films grown on GaAs (100) in the as-deposited state: (a) as-deposited Pt_2Ga on GaAs; (b) as-deposited PtGa on GaAs; (c) as-deposited $PtGa_2$ on GaAs.

film, since the signal-to-background ratio in the XRD patterns begins to increase as annealing temperature goes up. The diffraction patterns for the PtGa film annealed from 300°C to 600°C were essentially identical, but the signal-to-background ratio began to decrease. Annealing in an open system, such as in vacuum or under inert gas, may cause both $PtAs_2$ and GaAs to decompose thermally to produce gas phase As species. Therefore, in this case, the PtGa thin film starts to become Ga rich and $PtGa_2$ and Pt_3Ga_7 are produced, which coexist with PtGa and GaAs. Fig. 5 shows XRD patterns of a sample of $PtGa_2$ on GaAs heated to 100°C, 300°C, 450°C and 500°C, respectively, along with the pattern of an as-deposited film. The diffraction patterns for the sample were essentially identical up to 400°C. A new peak corresponding to the Pt_3Ga_7 (322) reflection begins to appear in XRD patterns of the sample annealed in the range of 450°C to 500°C. It is possible the $PtGa_2$ phase begins to react with extra Ga due to As evaporation from GaAs upon annealing.

Conclusions

Single phase thin films of Pt_2Ga, PtGa, and $PtGa_2$ have been successfully grown on GaAs by MBE. The results of annealing studies are in good agreement with the Pt-Ga-As ternary phase diagram. $PtGa_2$ and PtGa films are chemically stable on GaAs up to 450°C and 600°C, respectively. However, the Pt_2Ga films start

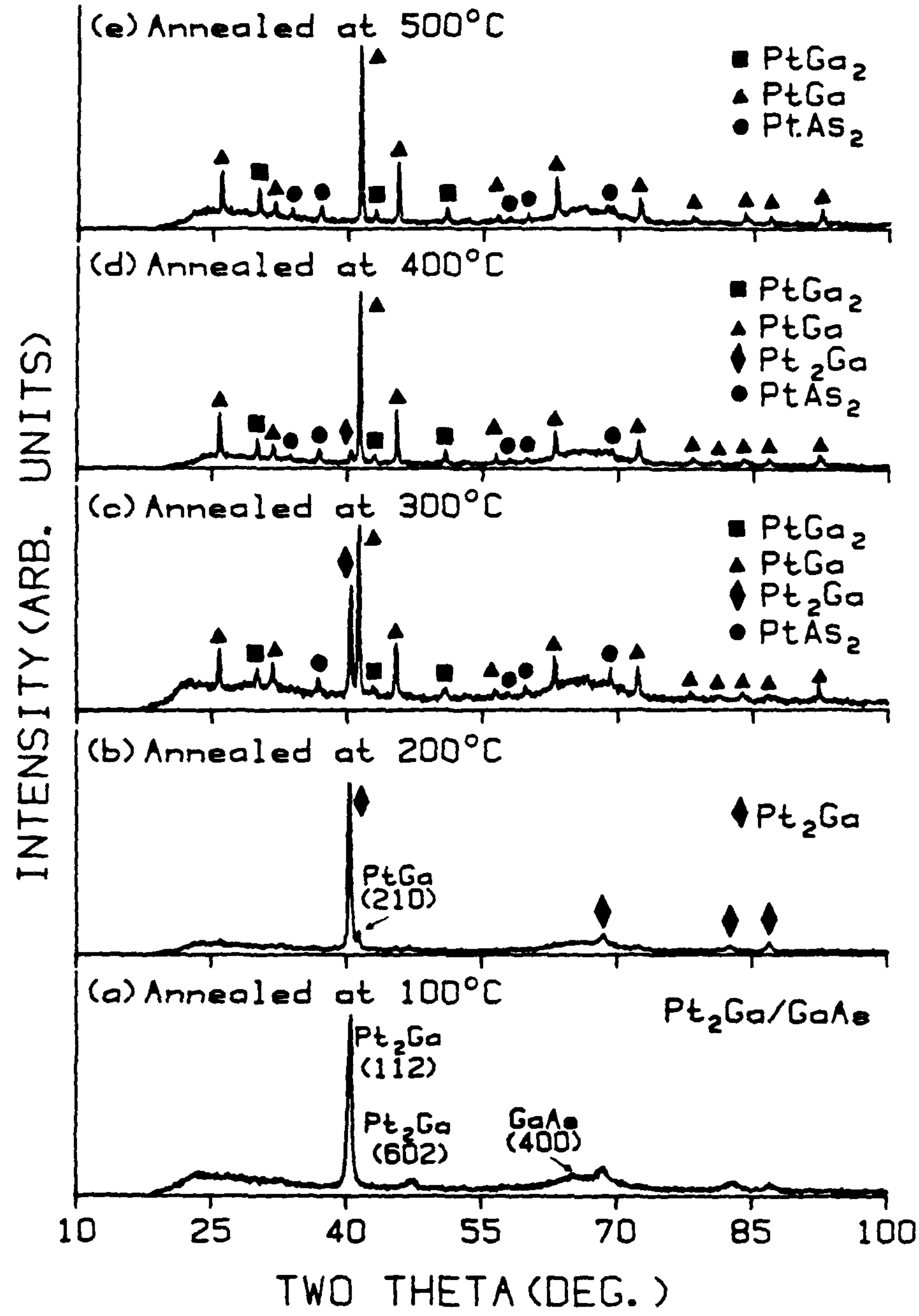

Fig. 3. XRD patterns of Pt_2Ga thin films on GaAs(100) for sample annealed to (a) 100°C, (b) 200°C, (c) 300°C, (d) 400°C and (e) 500°C.

to react with GaAs even at temperatures of 200°C to produce PtGa, $PtGa_2$, Pt_3Ga_7 and $PtAs_2$ at temperatures of 500°C. It has been shown here that the thermodynamics of bulk materials can be used to control the chemistry at the metal/semiconductor interface. In order to understand the Pt-Ga intermetallic system further, several additional studies including annealing studies under As ambient, temperature dependent TEM and transport measuremeants of various intermetallic Pt-Ga phases grown by MBE still need to be carried out.

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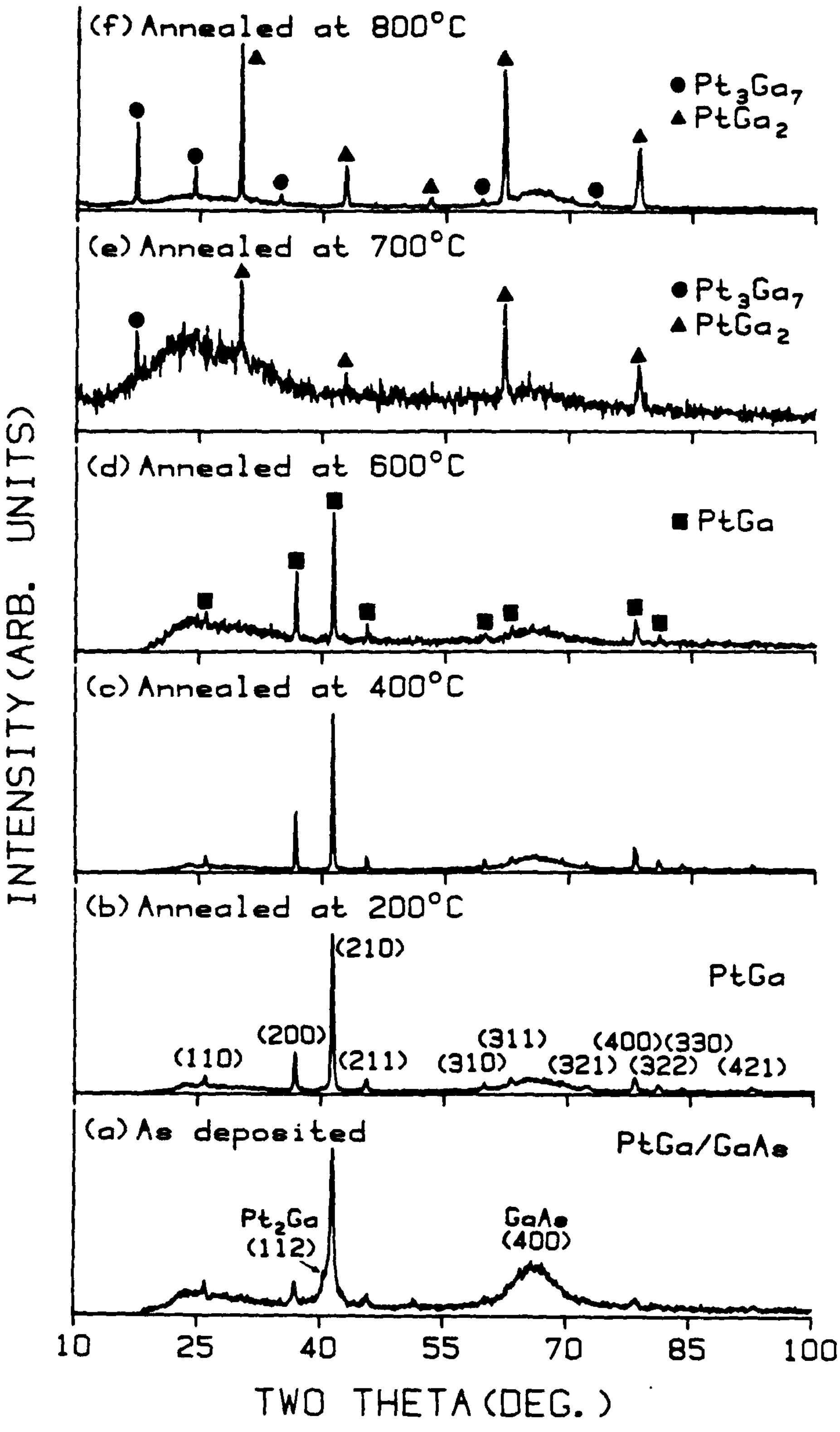

Fig. 4. XRD patterns of PtGa thin films on GaAs (100) for (a) the as-deposited film and after the sample was annealed to (b) 200°C, (c) 400°C, (d) 600°C, (e) 700°C and (f) 800°C.

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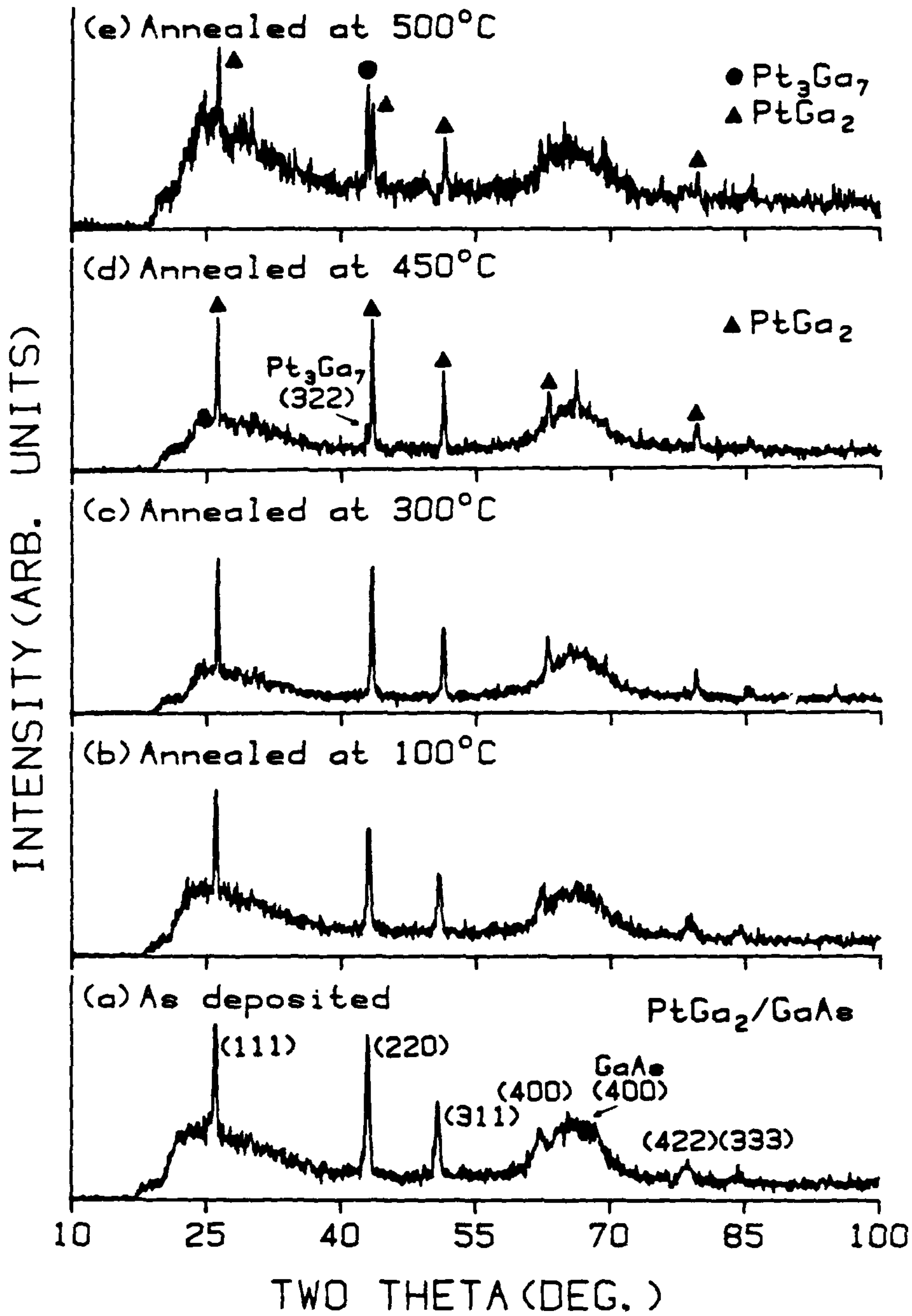

Fig. 5. XRD patterns of $PtGa_2$ thin films on GaAs (100) for (a) the as-deposited film and after the sample was annealed to (b) 100°C, (c) 300°C, (d) 450°C and (e) 500°C.

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